

Effect of Subphase Ca^{++} Ions on the Viscoelastic Properties of Langmuir Monolayers

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Abstract

It is known that the presence of cations like Ca^{++} or Pb^{++} in the water subphase alters the pressure-area isotherms for fatty acid monolayers. The corresponding lattice constant changes have been studied using x-ray diffraction. Reflection-absorption spectroscopy has been used to probe the chemical composition of the film. We report on the first measurements of the time evolution of the shear viscosity of arachidic acid monolayers in the presence of Ca^{++} ions in the subphase. We find that the introduction of Ca^{++} ions to the water subphase results in an increase of the film's viscosity by at least three orders of magnitude. This increase occurs in three distinct stages. First, there is a rapid change in the viscosity of up to one order of magnitude. This is followed by two periods, with very different time constants, of a relatively slow increase in the viscosity over the next 10 or more hours. The corresponding time constants for this rise decrease as either the subphase pH or Ca^{++} concentration is increased.

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I. INTRODUCTION

Over the last ten years there has been a renewed interest in the study of Langmuir monolayers [1], due to the development and application of a number of powerful tools like x-ray diffraction [2,3], Brewster Angle microscopy (BAM) [4,5], and fluorescence microscopy [6–8]. Langmuir monolayers are monomolecular films at the air-water interface formed by amphiphilic molecules. Typically, these molecules have a long hydrophobic chain oriented away from the water surface and a polar, hydrophilic headgroup that interacts with the components of the aqueous subphase. Langmuir monolayers serve as an excellent model for biological membranes and for surfactant stabilizers that are added to foams. Also, they are the starting point for Langmuir-Blodgett depositions where a solid substrate is passed through the Langmuir monolayers, transferring one or more layers of the molecules. For all three of these applications, understanding the interaction between Langmuir monolayers and ions in the subphase is important for two reasons. First, the ions are often naturally present in these systems, either as biologically relevant chemicals or as contaminants. Second, the ions provide a mechanism for controlling the mechanical properties of the films, which is especially important in applications related to foams and Langmuir-Blodgett depositions.

A number of techniques, including pressure-area isotherms [9–11], reflection-absorption spectrometry [12], and x-ray diffraction [13], have been used to study the effects of divalent cations on the monolayer structure. These studies have highlighted the important role played by pH, especially for fatty acid monolayers, in modifying the effects of divalent cations on the structure of the monolayer. The equilibrium phase behavior of fatty acids on a pure water, or low pH subphase, have been extensively studied [14]. There is a generally applicable phase diagram that consists of both “tilted” and “untilted” phases. A tilted phase is one in which the monolayer tails are tilted with respect to the surface normal. Generally, the untilted phases occur at higher pressures. One of the main effects of the calcium ions, as the pH is increased, is to lower the transition pressure between the various phases [13]. Ultimately, at very high pH, the tilted phases no longer appear to exist. This lowering of the transition pressure is often referred to as a “stiffening” of the monolayer. A common feature of these studies is that no long term variations in the monolayer properties were measured. This is reasonable if chemical equilibrium with the ions in solution is reached relatively rapidly.

Despite the evidence from pressure-area isotherms that the cations cause a stiffening of the monolayer, there has been minimal efforts to measure effects of cations on the viscoelastic properties of the monolayer [15,16]. In this paper, we report on a series of measurements of the viscoelastic properties of arachidic acid monolayers in the presence of Ca^{++} . We have looked at the effect of pH and Ca^{++} concentration on the time evolution of three properties of the monolayer: the isotherms; the viscosity (η); and the complex shear modulus G . Our isotherm results at $t = 1$ hr are consistent with previous measurements of fatty acids and divalent cations [13]. However, we have found a slow change in the viscoelastic properties of the monolayer over a long time period. This behavior suggests interesting kinetics for the chemical reaction between the arachidic acid and the Ca^{++} .

II. EXPERIMENTAL DETAILS

The viscoelastic properties were measured using a two-dimensional Couette viscometer that is described in detail elsewhere [17]. A schematic of the apparatus is given in Fig. 1. A circular barrier made of twelve individual teflon fingers is immersed into water in a circular trough. A circular knife-edge torsion pendulum (rotor) hangs by a wire so that it just touches the water surface in the center of the trough. A stationary teflon disk is placed in the water just under the pendulum. The disk has the same diameter as the knife-edge pendulum. A Langmuir monolayer is made at the annular air-water interface between the barrier and the rotor knife-edge. The barrier can be compressed or expanded to control the monolayer pressure and rotated to generate a two dimensional Taylor-Couette flow. The angular position of the rotor can be measured by means of a pick-up coil attached to the rotor. This is used to measure the torque generated by flow in the monolayer on the inner rotor. The torque provides a measurement of the monolayer viscosity. In addition, an external torque can be applied to the rotor by manipulating an external magnetic field. This allows for both oscillatory measurements of the linear shear response of the monolayer and measurements of stress relaxation curves for monolayers.

The apparatus is also equipped with a Brewster Angle Microscope (BAM) for observation of the domain structure of the film. The BAM image measures the relative reflectivity of p-polarized light incident on the monolayer at the Brewster angle for pure water. Variations of reflectivity of the monolayer correspond to changes in the orientation of the tilted molecules from domain to domain.

To study the effect of cations, it is imperative to start with water that has minimal ionic content. We achieved this by passing de-ionized water through a Millipore filter to obtain water with resistivity in excess of 18 M Ω /cm. The concentration of Ca^{++} was set by adding $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to the purified water. Most of the experiments used a 0.65 mM Ca^{++} concentration so that the results would be comparable with Ref. [13].

The arachidic acid monolayer was made from a chloroform solution. The solution was placed on the aqueous subphase with a microsyringe and allowed to relax for about 20 minutes to facilitate the evaporation of the solvent. Then it was compressed to the pressure of 9 dyne/cm. All the data presented here were taken at 22 °C. At this temperature and pressure, the monolayer is in the L_2 phase. One hour after the solution was placed on the subphase, the equilibrium angle, θ_1 , of the rotor was measured. The outer barrier was set into rotation to generate a Couette flow. The Couette flow causes a torque τ on the rotor displacing it to a new equilibrium position θ_2 such that $\tau = \kappa(\theta_2 - \theta_1)$, where κ is the torsion constant of the wire. After rotating the barrier for about 5 minutes to achieve equilibrium, θ_2 was measured, and then the rotation was stopped. This series of experiments was repeated every hour. The isotherms as well as the complex shear modulus were measured separately. The barrier rotation rate was 0.0237 rad/sec. With $R_{\text{inner}} = 3.81$ cm and $R_{\text{barrier}} = 6.5$ cm, this corresponds to a shear rate of 0.057 s^{-1} . G was measured at $\omega = 0.251$ rad/sec.

III. RESULTS

Figure 2 shows the time evolution of viscosity (measured by the Couette flow method and henceforth referred to as η) for different concentrations of Ca^{++} in the subphase. All of

the measurements were done at pH 5.5. There are two points of note. One, the higher the concentration, the higher the rate of viscosity rise. Secondly, the rise in viscosity is in three parts. There is an initial jump of about one order of magnitude within the first hour. The next two periods are separated by $\eta = 1$ g/s, below and above which the viscosity clearly rises with different slopes on the semilog plot. This indicates there are three time constants associated with the increase. As the first data point is taken after one hour of making the film, we cannot comment about the time constant for the viscosity rise in the first stage, except that the upper limit for τ_1 is about 0.5 hour. It should be noted that both the time constants decrease with increasing concentration. For the film with 0.65 mM concentration of Ca^{++} , $\tau_2 = 1.76$ hour and $\tau_3 = 5.43$ hr, where τ_2 and τ_3 are the time constants for the second and the third stage respectively. The time constants for the rest of the data are given in the figure caption.

The three different stages of viscosity rise are also obvious in Fig. 3 which depicts the dependence of this rise on the subphase pH. Note that below pH = 4, the viscosity is small and almost constant. This is consistent with other studies where the isotherms were seen to remain unchanged for about the same pH. As the pH values are increased, both the initial jump in viscosity and the later rates of rise increase.

The results of the oscillatory experiment are plotted in the Fig. 4. The complex shear modulus $G (=G' + iG'')$ is known to depend on the strain amplitude for some Langmuir monolayers [18]. Here G' is the elastic component of the shear modulus and G'' is the viscous component. For a linear viscoelastic fluid, the relation between G'' and the viscosity, η , is given by $G'' = \omega\eta$, where ω is the oscillation frequency. In this case we found G'' to be weakly and G' to be strongly dependent on the strain amplitude. The dependence was qualitatively the same as in Ref. [18] i.e., G was constant at small amplitudes and decreased for higher amplitudes. To ensure linear response, we measured G at a small constant strain amplitude of about 10^{-3} . As with η , G'' displays two distinct periods of increase after the first hour. However, G' rises monotonically with time.

Figure 5 shows the variation of the arachidic acid monolayer isotherm as a function of time for pH = 5.5. It must be noted that the isotherms were measured separately from the viscosity. There might be some differences in the rate of Calcium attachment arising from the fact that there was no rotation of the monolayer or generation of circular flow in the subphase. But, the effect is bound to be minimal for two reasons. First, the flow during viscosity measurements only occurred for roughly 10% of the data run. Second, there was no turbulence during the flow, so the rate of mixing in the subphase would not be substantially modified. Furthermore, the qualitative behavior of G'' was found to be the same when measured with the rotation as it was when measured without rotation. This confirmed that the rotation had minimal effect on the Ca^{++} binding rate. Figure 5 also shows the position of the kink in the isotherm that corresponds to the 2nd order phase transition for arachidic acid monolayer without Ca^{++} in the subphase (horizontal dashed line). The presence of Ca^{++} does alter the isotherm in the first hour. There is a lowering of the pressure at which the 2nd order transition occurs by about 4 dyne/cm. This is consistent with the isotherms published in the literature [13]. From the X-ray data it is known that this change is due to the bound calcium changing the head group interactions so that the molecules come closer together. However, after this initial drop, there is a slow change in the isotherm. This change corresponds to a decrease in the transition pressure by about 0.3 dyne/cm/hour.

The kink also appears to become more rounded with time. However, we believe that the apparent rounding is due to the high viscosity of the film and is not a real effect.

IV. DISCUSSION

In summary, we find that there are many effects of Ca^{++} ions on the arachidic acid monolayer. In the first hour, the isotherm shifts downwards in pressure by about 4 dyne/cm. Over the next ten hours, it changes by about 3 dyne/cm. These drops are accompanied by changes in viscosities, measured by either the rotating barrier method or the oscillating rotor method. One can interpret the viscosity rising during the first hour as a direct result of the change in the head group interactions. This is consistent with the pH data. It is known that sufficiently low pH suppresses the binding of divalent ions to the monolayer [12,13,19,20], and we observe no viscosity increase at pH 3.4 and below.

The slow rise associated with the late time evolution of the viscosity is surprising. The 3 dyne/cm drop in the transition pressure in this period suggests a very slow rate of Calcium ionically binding to the carboxylate. For octadecanoic acid monolayers, IR reflection-absorption studies [12] have shown that near pH = 6, the Ca^{++} does not bind to all the molecules but that some undissociated acid molecules remain in the film. The increase in the viscosity, taken together with the slow change in the isotherm suggest that the same is true for the arachidic acid and that these remaining acid molecules slowly bind with the Ca^{++} ions with a time constant of a few hours. This is supported by the fact that the time constants τ_2 and τ_3 both decrease with increasing subphase Ca^{++} concentration. The steady rise of G' seen in Fig. 4 is consistent with this picture; however, the existence of a single time constant needs to be explained.

The presence of two different time constants, namely τ_2 and τ_3 , is also puzzling. If we accept that Ca^{++} continues binding to the monolayer, then two broad possibilities emerge:

- a. that the rate of the binding changes abruptly and this change is reflected in the viscous response or
- b. that the rate of binding does not change but the rate of viscosity rise with respect to bound site concentration varies after reaching a critical value.

At this point, it is difficult to say which of these pictures is more accurate, but both are interesting. If the first case is correct, it suggests interesting long-term kinetics associated with the chemical reaction mechanism that undergo abrupt changes. If the latter reason is correct, it suggests an interesting interplay between the microscopic structure of the monolayer and the macroscopic viscosity.

One possible mechanism for the abrupt change in the evolution of the viscosity is the contribution of the line tension between domains in the monolayer to the viscosity. It is known from foams and other complex fluids that line tension (or surface tension in three dimensions) can substantially alter the macroscopic viscosity of a fluid. The L_2 phase of arachidic acid consists of a random domain structure. Friedenbergh, et al. [21] report that for docosanoic acid monolayers in the L_2 phase, domains stretched by an extensional flow do not relax back to their original shape. This indicates that the line tension in the absence of Ca^{++} is nearly zero. Similar behavior is observed for our samples of arachidic acid. However, with Ca^{++} ions in the subphase, our BAM images show evidence of domain relaxation. Presumably, line tension between domains will be dominated by Ca^{++} absorption at the

domain boundaries. If this saturates, the rate of change of the viscosity would be altered. We are currently undertaking detailed studies of this behavior to probe the impact of the line tension to the overall viscoelastic response of the monolayer and the effect of Ca^{++} ions on the line tension.

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FIGURES

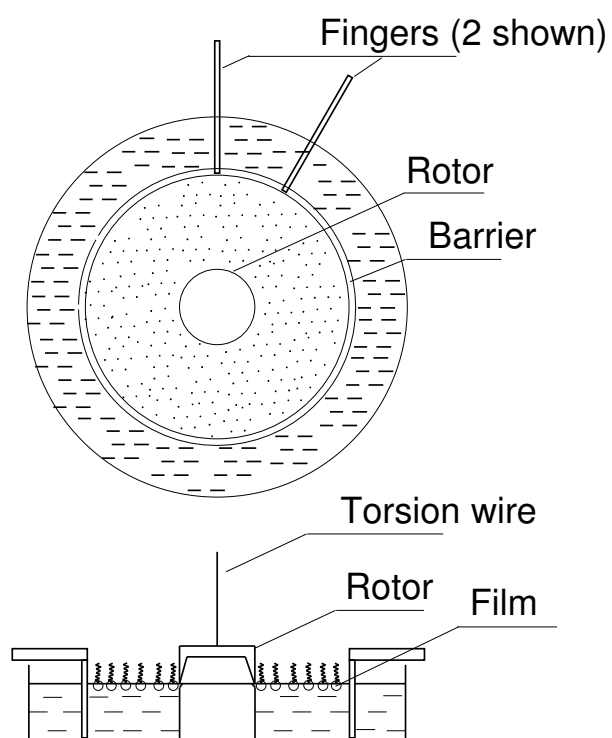


Figure 1: R. S. Ghaskadvi and Michael Dennin, J. Chem. Phys.

FIG. 1. Schematic drawing of the apparatus.

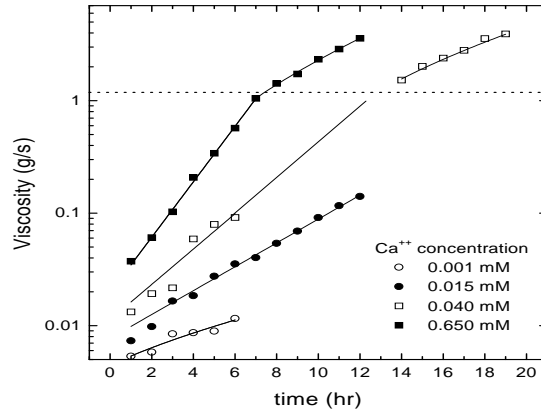


Figure 2: R. S. Ghaskadvi & Michael Dennin, J. Chem. Phys.

FIG. 2. The viscosity of the arachidic acid monolayer as a function of time at 22°C. The different curves correspond to different concentrations of Ca^{++} ions at pH 5.5. The solid lines corresponds to the least square fits to the equation $y = Ae^{x/\tau}$. Fit values 0.001 mM : $A=0.0043$ g/s, $\tau_2=12.77$ hr; 0.015 mM : $A=0.0077$ g/s, $\tau_2=4.10$ hr; 0.04 mM : $A=0.0162$ g/s, $\tau_2=2.76$ hr, $\tau_3=8.36$ hr; 0.65 mM : $A=0.0197$ g/s, $\tau_2=1.76$ hr, $\tau_3=5.43$ hr.

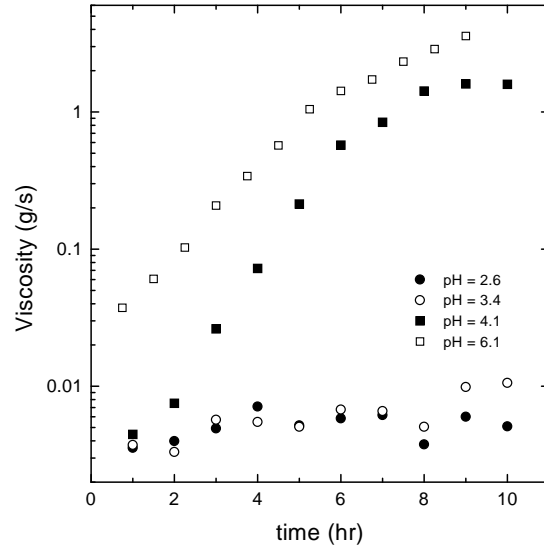


Figure 3: R. S. Ghaskadvi & Michael Dennin, J. Chem. Phys.

FIG. 3. The viscosity of the arachidic acid monolayer as a function of time at 22°C, $\Pi = 9$ dyne/cm. The different curves correspond to different pH values of the subphase. The concentration of the Ca^{++} ions is fixed (0.65 mM).

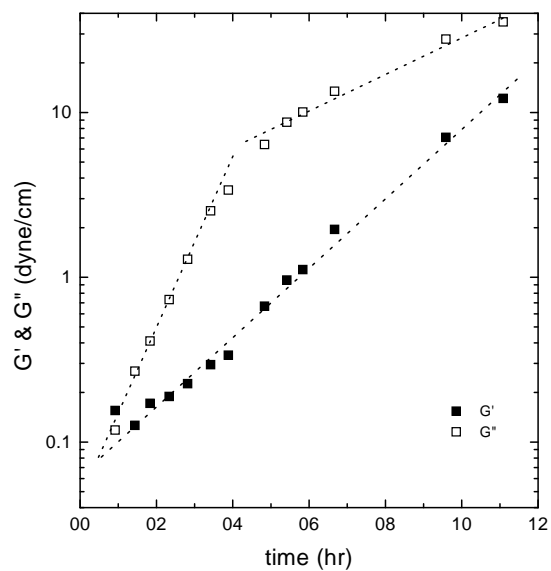


Figure 4: R. S. Ghaskadvi & Michael Dennin, J. Chem. Phys.

FIG. 4. G' and G'' of the arachidic acid monolayer as a function of time at 22°C, $\Pi = 9$ dyne/cm. The dotted lines are guides to the eye.

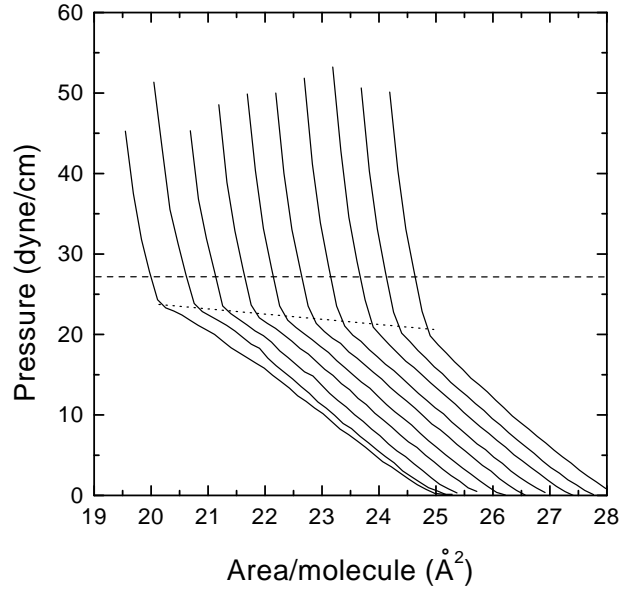


Figure 5: R. S. Ghaskadvi & Michael Dennin, J. Chem. Phys.

FIG. 5. Isotherms of arachidic acid monolayer at 22°C , subphase $\text{pH} = 5.5$, and subphase Ca^{++} concentration of 0.65 mM . The x-axis reading is accurate for the first isotherm only since the rest are shifted for the sake of clarity. The isotherms are taken one hour apart. The dotted line is drawn to guide the eye along the kink position. The dashed line represents the pressure at which the kink occurs for the monolayer without Ca^{++} in the subphase.